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INDUSTRIAL WASTE GUIDE

BY-PRODUCT COKE

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INDUSTRIAL WASTE GUIDE - BY-PRODUCT COKE

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INDUSTRIAL WASTE GUIDE - BY-PRODUCT COKE

This Guide supplements the earlier work published as a part of the Ohio River Pollution Control Report (1). Results are summarized herein for industrial waste surveys conducted by the Public Health Service at eight different by-product coke plants. Taste and odor studies, and bio-assays of coke plant wastes are included. Emphasis has been placed on definition of the problem, pollutional effects, remedial measures, and methodology.

MAGNITUDE OF PROBLEM

The first by-product coke plant in the United States was erected in 1892 by Semet-Solvay at Syracuse, New York and consisted of 12 ovens. On January 1, 1955 there were 82 by-product coke plants in the United States with some 15,000 ovens having an annual capacity of 78.6 million tons of coke. During the year 1954, there were 58 million tons of by-product coke produced, of which 52 million tons were used for blast furnace operations. Approximately 77 per cent of this coke was produced in the six states of Pennsylvania, Ohio, Indiana, Alabama, New York, and West Virginia with the relative rank of production being in the same order (2). Based on this level of operation, it can be conservatively estimated that 30 tons of phenol per day are produced in the untreated liquid wastes from by-product coke plants. Toxicity of these wastes is another major problem.

DESCRIPTION OF PROCESS

By-product coke is produced by heating bituminous coal in closed ovens out of contact with air and recovering the volatile products that are evolved. The ovens are constructed of silica brick and are arranged side by side in groups of thirty or more, each group being referred to as a battery. Modern ovens are about 40 feet long, 10 to 14 feet high, and 14 to 18 inches wide with a capacity of 10 to 22 tons of coal each. The ovens are heated by burning either coke oven

or blast furnace gas in flues constructed in the oven walls.

The quality of the coke and the quality and quantity of coal chemicals and gas are controlled by blending various types of high-volatile and low-volatile bituminous coals of the coking type. There is no precise formula but a typical blend would be 70 per cent high-volatile and 30 per cent low-volatile coal. Low ash, low sulfur coal is preferred. In general it is advantageous to charge a low moisture coal, 4 to 5 per cent water, because of the additional heat required to vaporize the water. Coal is charged through small openings in the top of the ovens by means of hopper bottom cars that travel on tracks located on top of each battery. The coking period is normally 16 to 24 hours with flue temperatures varying between 1800° F. and 2600° F. depending on the type of coke being produced. When carbonization is complete, the doors forming each end of the oven are removed and a pushing machine, equipped with a powerful ram, pushes the incandescent coke into the quench car. The quench car is quickly moved to a quench station where the coke is cooled by water sprays.

Volatile products of the coal leave the top of the ovens through standpipes which connect with a large gas collecting main extending the length of the battery. Initial cooling of the gases takes place in the collecting main where they are contacted with sprays of flushing liquor which liquor has previously condensed from the gas. The origin of this condensate is the moisture in the coal and the water produced by decomposition of the coal, i.e., water of constitution. The gases then pass through primary coolers which may be either of the direct or the indirect type. The flushing liquor, carrying about 85 per cent of the tar, and the primary cooler condensate drain to one or more decanters for separation of the tar and liquor (Figure 1). Liquor condensed from the gases, referred to as ammoniacal liquor, is passed through an ammonia still for recovery of ammonia.

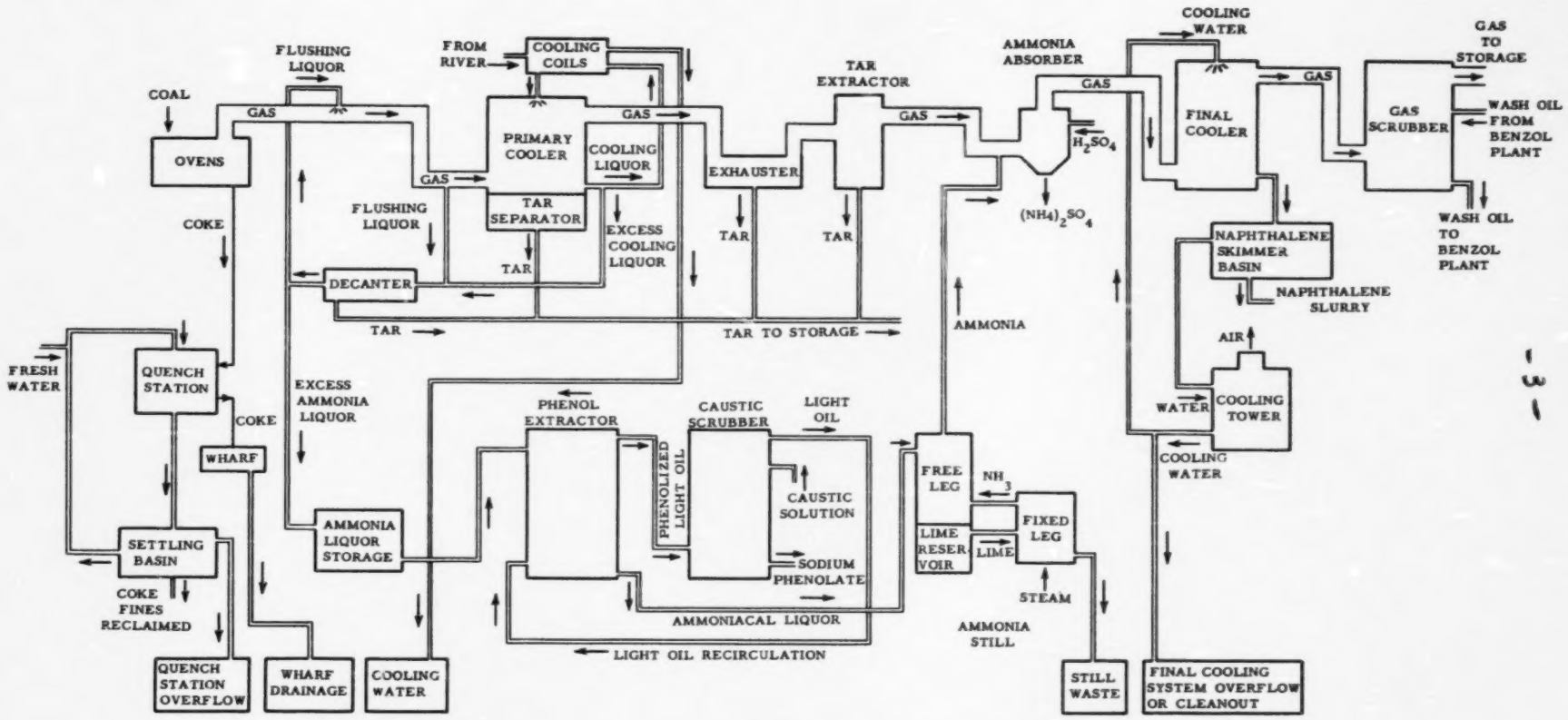


FIGURE 1

SIMPLIFIED FLOW DIAGRAM

BY—PRODUCT COKE PLANT

SHOWING LIQUID WASTES SOURCES

Pertinent data for raw ammoniacal liquor at seven coke plants are shown in Table 1.

Ammonia Recovery Processes

Two processes are used in the United States for recovery of ammonia from coke-oven gas. These are referred to as semidirect and indirect. Approximately 85 per cent of the ammonia produced in coke plants is recovered as ammonium sulfate by the semidirect process (3). Recently some plants are producing ammonium phosphate. The balance is produced as concentrated ammonia liquor by the indirect process.

In the semidirect process, only a portion of the ammonia is dissolved in the ammoniacal liquor and the remainder stays in the gas. The volume of raw ammoniacal liquor produced by the semidirect ammonia recovery process varied between 17 and 28 gallons per ton of dry coal for the coke plants studied. The ammonia is distilled from the liquor and returned to the gas stream. The gas is then passed through an exhauster, a tar extractor, and a weak sulfuric acid bath (absorber) to produce ammonium sulfate. Pyridine bases are recovered from the mother liquor of the sulfuric acid ammonia absorber at some plants.

The indirect system substitutes a series of ammonia scrubbers for the sulfuric acid absorber. Ammonia is scrubbed from the gas by a countercurrent water wash. The ammonia concentration in the scrubber water is increased by circulating it through one or more compartments of the direct-type primary cooler (4). The ammonia scrubber water and primary cooler condensate combine to give ammoniacal liquor. The volume of ammoniacal liquor produced by the indirect ammonia recovery system normally ranges between 60 and 90 gallons per ton of dry coal. This ammoniacal liquor is passed through an ammonia still to recover the ammonia as a concentrated ammonia liquor.

TABLE I.
RAW AMMONIACAL LIQUOR CHARACTERISTICS AND VOLUME
CORRELATED WITH DESIGN AND OPERATIONS

AMMONIA RECOVERY PROCESS		SEMIDIRECT AMMONIA RECOVERY							INDIRECT AMMONIA RECOVERY	
Plant *		A-1	A-2	A-3	B	C	D	E-2	F-2	H-2
Phenols	Pounds Per 1000 Tons Dry Coal	300	130	160	250	80	250	280	1200	380
Cyanide (CN)		—	7	—	3	6	6	26	34	120
Total NH_3 (N)		—	890	—	490	470	1080	2400	5530	—
Flue Temperature	°F	2300	2470	2400	2325	2500	2550	2020	1740	2390
Volatile Matter	Per Cent	29.8	30.5	31.3	35.4	25.7	29.0	28.0	25.2	30.9
Coal Moisture		—	5.7	6.3	4.5	4.9	4.4	4.5	8	4.5
Volume	Gallons Per Ton Dry Coal	17	18	19	21	18	21	28	72	52

* Plants designated A-1, A-2, etc. are the same plant at which two or more surveys were made under different operating conditions.

Light Oil Recovery

Coke oven gas contains approximately one per cent light oil vapors by volume. Gas leaving the ammonia scrubbers of the indirect ammonia recovery system is at a suitable temperature for recovery of these light oils. However, gas leaving the ammonia absorber of the semidirect system is at a temperature of about 145° F. and must be cooled to 85° F. or lower for recovery of the light oil. This cooling is accomplished in a hurdle-packed tower (final cooler) by direct contact with water flowing countercurrent to the ascending gas. Practically every coke plant has a recirculation system for this final cooler water employing either a cooling tower or a spray pond. Evaporation normally exceeds the quantity of water condensed from the gas. Cooling coils may be used in lieu of cooling towers, when their operation might cause objectionable air pollution, in which case the condensate is sewered. Naphthalene is condensed from the cooled gas in the form of crystals and is continuously removed from the gas final cooler water.

Light oil is scrubbed from the cooled gas by a high boiling wash oil. The light oil is then distilled from the wash oil and the wash oil is cooled and recirculated. This light oil is refined by stills and fractionating columns (Figure 2). Benzene, toluene, and the xylenes are the principal constituents of light oil. There are a large number of other compounds present in smaller amounts.

Coke Quenching

The incandescent coke must be promptly cooled by water sprays to prevent combustion. This quenching operation is automatically controlled and requires between one and two minutes. The time is adjusted so that most of the fire is extinguished but sufficient heat is retained in the mass of coke to evaporate the larger portion of the entrained water.

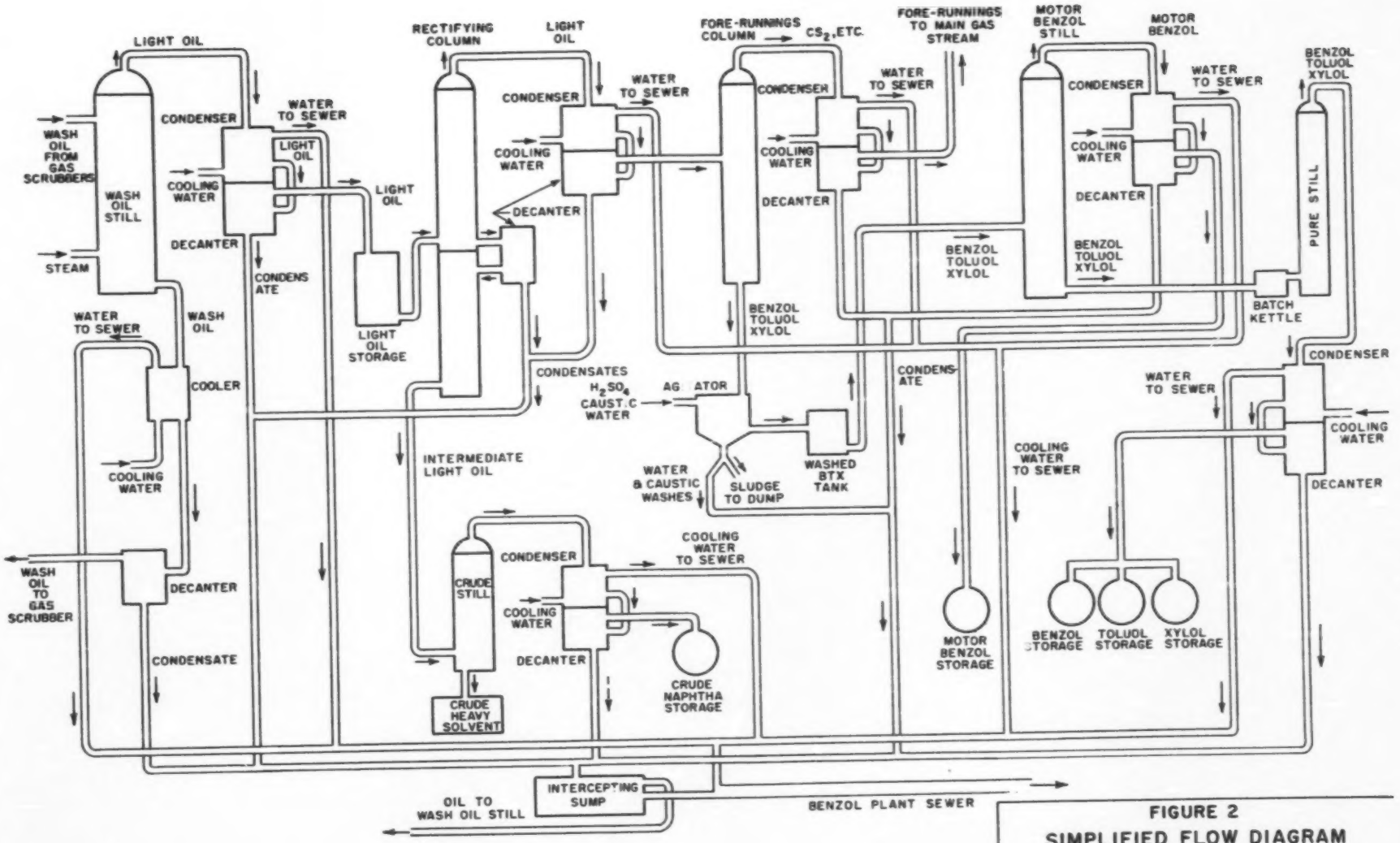


FIGURE 2

SIMPLIFIED FLOW DIAGRAM

LIGHT OIL RECOVERY AND REFINERY

SHOWING LIQUID WASTE SOURCES

RAW MATERIALS AND PRODUCTS

The yields and characteristics of the carbonization products depend primarily on the amount of volatile matter in the coal and the severity, duration, and nature of the heat treatment. Other variables believed significant but not fully evaluated are:

1. Type and preparation of coal
2. Oven design and charging practice (Space above coal)

Carbonization of coal results in relatively few major products. However, from these products, some of which are available economically from no other source, stem hundreds of other chemicals and literally thousands of end products.

The normal ranges for raw materials and products, per ton of dry coal carbonized, are listed below:

Raw Material	Lbs./Ton
Sulfuric Acid, 66°Be.	17 - 27
Sodium Hydroxide	0.2 - 0.5
Lime	1.0 - 1.8
Principal Products	**Quantities/Ton**
Coke, lbs.	1300 - 1550
Gas, cu. ft.	10,000 - 12,500
Tar (Crude), gal.	5 - 12
Ammonia (NH_3), lbs.	4 - 7
Light Oil (Crude), gal.	2 - 4
Pyridine (Crude), gal.	0.014
Naphthalene from Final Coolers and Benzol Plant, lbs.	1.6

VOLUME AND CHARACTER OF WASTES

The most important liquid wastes discharged from a by-product coke plant are ammonia still waste and benzol plant wastes. The latter are more accurately referred to as light oil recovery and light oil refining wastes. Gas final cooler water is usually recirculated but any overflow constitutes a highly pollutional waste. Quench water and cooling water add materially to the volume but ordinarily do not contribute significant pollution. There are always some residual wastes originating from equipment maintenance, inevitable leaks, and process irregularities.

Ammonia Still Waste

Ammonia still waste is the liquor resulting from steam stripping ammonia from raw ammoniacal liquor. The volume of still waste is 20 to 40 per cent greater than the volume of raw liquor feed, because of condensate from steam applied directly to the still and milk of lime added to decompose fixed ammonia. The volume of ammonia still waste per ton of coal carbonized varies significantly at different plants as indicated in Table 2. The influencing factors are:

1. Ammonia recovery process
2. Moisture of coal - usually 4 to 6 per cent
3. Water produced by decomposition of coal
4. Steam used in the still (wet or dry)
5. Milk of lime used in the ammonia still

The composition of ammonia still wastes is related directly to the volatility of the coal carbonized, to coking temperature, and to design and operation of the various units. Comparison of the phenol content in the raw ammoniacal liquor for Plants C and D, Table 1, gives a striking example of the influence of volatile matter on the liquor. Likewise in Table 2, the coal

TABLE 2
AMMONIA STILL WASTES CHARACTERISTICS AND VOLUME
CORRELATED WITH DESIGN AND OPERATIONS

AMMONIA RECOVERY PROCESS		SEMIDIRECT				INDIRECT					
DEPHENOLIZATION SYSTEM		VAPOR RECIRCULATION			BENZOL EXTRACTION	NONE					
Plant *		A-1	A-2	B	C	D	E-1	E-3	G	H-1	H-2
Phenols	Pounds Per 1000 Tons Dry Coal	46	7.3	48	7.4	230	72	120	640	475	320
Cyanide (CN)		0.4	4.5	0.9	2.9	1.0	0.4	5.2	2	2.4	6.3
Thiocyanate (SCN)		—	57	230	66	—	—	240	—	—	500
Total NH_3 (N)		7.1	5.7	28	14	80	870	—	52	55	—
Sulfides (H_2S)		69	—	—	4	8	—	—	33	32	—
Chloride (Cl)		—	—	420	—	1800	—	—	1700	—	—
5-Day BOD		150	—	280	—	470	370	—	1200	1400	—
Volume	Gallons Per Ton Dry Coal	20	21	27	23	33	20	24	110	60	68
Flue Temperature	°F	2300	2470	2325	2500	2550	2250	2200	2460	2390	2390

* Plants designated A-1, A-2, etc. are the same plant at which two or more surveys were made under different operating conditions.

volatility for H-1 was 34.9 per cent and for H-2 it was 30.9 per cent. Tar production at Plant C was the lowest for the plants studied. This low tar yield was associated with the lowest phenols observed in the ammoniacal liquor (Table 1).

The Bureau of Mines has demonstrated that the production of tar and the per cent of tar acids in the tar both decrease progressively with increasing temperature of carbonization (5). The effect of coking temperatures on production of tar acids (phenols) is illustrated by Figure 3. In like manner the phenol

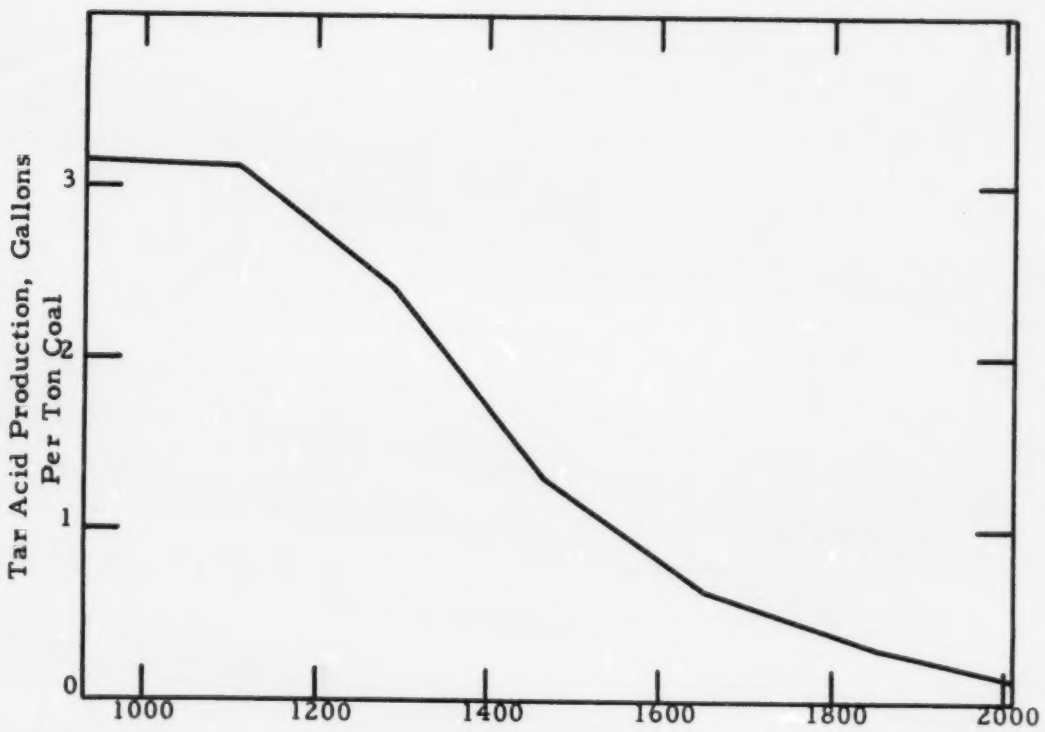


FIGURE 3 - TAR ACID PRODUCTION
AT DIFFERENT COKING TEMPERATURES
(Pratt Unwashed Coal)

content of ammoniacal liquor varies directly with the coking temperature (Figure 4). This curve shows variations in phenol in the ammoniacal liquor for the same coke plant operating at different coking temperatures. These data indicate that within a relatively narrow temperature range, phenol production may vary as much as 200 to 300 per cent.

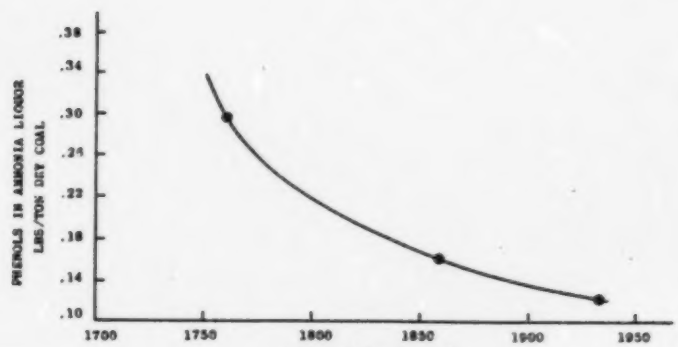


FIGURE 4 - VARIATION OF PHENOL IN AMMONIACAL LIQUOR AT DIFFERENT OVEN TEMPERATURES AT PLANT A

Comparison of phenol unit values for the indirect and the semidirect ammonia recovery plants (Tables 1 and 2) affords an excellent illustration of the influence which the volume of ammoniacal liquor has on the amount of phenolic constituents dissolved from the tar. This is an example of the distribution of a solute between two immiscible solvents. Phenol in the ammoniacal liquor for Plant H was significantly lower than the other indirect ammonia recovery plants. This was attributed to the fact that a separate tar decanter was provided for the flushing liquor. The primary cooler condensate and the ammonia scrubber water at Plant H were combined and passed through a second decanter. Provision of a separate tar decanter for flushing liquor at the semidirect ammonia recovery plants

should likewise reduce to a minimum the takeup of tar acids (phenols) from the tar.

The ammoniacal liquor of the indirect ammonia recovery plants absorbs more HCN from the gas than it does in the semidirect process because of the larger volume and lower temperature. The ammonia still effluent was the principal source of cyanide waste from the indirect plants. Some HCN distills over with the ammonia into the ammonia water concentrate. There is a strong tendency for thiocyanates to form in the ammoniacal liquor from HCN in the presence of sulfides and free ammonia. Thiocyanates have been reported as high as 2000 ppm in the ammonia still waste.

Most of the ammonia in raw ammoniacal liquor is present as either "Free" or "Fixed" ammonium salts. Free salts are readily decomposed by boiling whereas the "Fixed" salts must be boiled with an alkali. The effluent from a properly operated ammonia still should not contain in excess of 500 ppm ammonia and normally will be less than 300 ppm.

Light Oil Recovery and Refinery Wastes

Benzol plant operations vary in different plants but the basic processes are similar. Condensed steam from stripping operations, and cooling waters, constitute the bulk of the liquids going to the sewers. There is little, if any, carryover of moisture from the gas scrubbers to the benzol plant. The volumes of liquid wastes discharged from benzol plants vary considerably depending on whether or not cooling water is recycled or is discharged directly to the sewer. Flow data obtained at five plants, which included cooling water, showed values from 375 to 750 gallons per ton of dry coal. At three other plants, where the cooling water was either recycled or discharged to a differ-

ent sewer, the benzol plant discharge varied from 20 to 89 gallons per ton of dry coal.

When water comes in direct contact with the process stream, a certain amount of soluble material is absorbed by the water. There is usually a condenser and a decanter for the overhead from every distilling column. The discharge from these decanters and the agitator wastes, are the chief sources of pollutants in the benzol plant. Minor quantities of wastes are released from wash oil cleaning operations and storage tank drains. Some benzol plants discharge residue removal column tailings to the sewers.

Table 3 shows the effects of the type of operation on benzol plant wastes. The concentration of phenol in a scrubbing water is one of the factors that determines the amount of phenol which it will absorb. Thus, the vapor pressure of phenol in fresh water would be zero and this water would tend to absorb more phenol from a gas stream than recirculated water which already contained phenol. The indirect ammonia recovery system scrubs the gas stream with fresh water, and, in addition to removing almost all of the ammonia from the gas, the scrubber water is effective in absorbing phenol. A similar situation exists in Plant E in the once-through final cooler. The carryover of phenol in the gas to the benzol department, in the semidirect ammonia recovery systems, is clearly illustrated in Table 3.

The debenzolized wash oil from the still is cooled and any contained water is separated before returning it to the scrubber. The water may be decanted before and/or after the coolers. In addition to light oil, wash oil absorbs tarry particles, complex unsaturated organic compounds, hydrogen sulfide and other sulfur compounds, and phenols. They react with each other to produce gummy or tarry materials which form muck. This muck inhibits light oil re-

TABLE [illegible].

BENZOL PLANT EFFLUENT
CORRELATED WITH DESIGN AND OPERATIONS

AMMONIA RECOVERY PROCESS		SEMIDIRECT						INDIRECT	
GAS FINAL COOLER SYSTEM		COOLING TOWER AND RECIRCULATION (CLOSED SYSTEM)					COOLING WATER DIRECT TO SEWER	NONE	
DEPHENOLIZATION SYSTEM		VAPOR RECIRCULATION		BENZOL EXTRACTION		NONE			
Plant		A-2	B	A-3	C	D	E-2	H-1	H-2
Phenols	Pounds Per	11	56	29	6	7	0.09	1	0.5
Cyanide (CN)	1000 Tons	3.1	8.7	—	1.9	1.5	0.02	—	5.0
Total NH_3 (N)	Dry Coal	9.4	12	—	—	1.2	0.05	5.0	14
Phenol in Ammoniacal Liquor	ppm	850	1410	1020	550	1480	1210	—	880

covery and must be removed intermittently from decanters or continuously in steam heated wash oil purifiers. It is boiled with steam to break emulsions. The good oil is then separated by decantation and the water and residue are discarded to the sewer.

The characteristics of decanter discharge depend largely on the volumes of steam used and the nature of the process material. The amounts of materials dissolved in the water again depend on relative solubilities. Partial analysis of three decanter effluents at one plant, employing a rectifying column after the stripping still, are shown in Table 4.

TABLE 4

CONCENTRATIONS OF WASTE CONSTITUENTS IN DECANTER EFFLUENTS AT ONE LIGHT OIL RECOVERY AND REFINING PLANT

Waste Constituent	Primary (1) Decanter ppm	Intermediate (2) Decanter ppm	Secondary (3) Decanter ppm
Phenols	420	240	29
Cyanide (CN)	4.5	7.8	240
Sulfides (H_2S)	1.4	5.3	150
Thiocyanate (SCN)	24	3.1	4.0
5-Day BOD	1040	870	360
pH	6.9-7.3	7.7-7.9	6.5-6.6

(1) After wash oil still condenser.

(2) On line of heavy fraction of light oil between bottom and top of rectifying column.

(3) On overhead line of rectifying column, after condenser and prior to forerunnings column.

Light oil is treated with sulfuric acid in a lead lined agitating tank to remove sulfur-containing and unsaturated organic compounds. The consumption

of 66° Be. acid usually ranges between 0.4 and 0.8 lb. per gal. of light oil washed. The acid is added in two or more washes. The reactions between the sulfuric acid and organic compounds are complex and the gummy materials formed are removed in the form of sludge. It is common practice to wash the acid treated light oil with water (approximately 0.1 gal. water/gal. light oil) before neutralizing with alkali.

It is customary to dispose of the spent acid and sludge on dumps or occasionally by burning. Recovery and reuse of the acid is possible but is not economically sound. With few exceptions, rinse water and spent caustic are discharged to the sewers through the intercepting sump.

Gas Final Cooler Water

Gas final cooler water constitutes a serious pollution threat at all by-product coke plants. This cooling water comes in direct contact with the gas and is a potential source of highly toxic cyanogen compounds in coke plant effluents. Hydrogen cyanide (HCN) is the principal cyanogen compound in coal gas. High temperature carbonization produces considerably more cyanide than low temperature coking. This is reflected in Table 5 for studies E-1 and E-2. It is formed in coke ovens by the reaction of ammonia with carbon or such carbon compounds as acetylene.

Hydrocyanic acid is an extremely water soluble compound and accordingly may be expected in water condensed from the gas and other water that has been in contact with the gas. Its low boiling point (26°C.) and correspondingly high vapor pressure result in relatively rapid volatilization from dilute aqueous solutions, at a normal pH range, when agitated and exposed to the atmosphere.

Cooling of coke oven gas in the final cooler condenses about 5 gallons of water from the gas per ton of dry coal carbonized. Plants employing closed

systems, and adiabatic evaporation in a cooling tower, use 250 to 500 gallons of water in the final cooler per ton of coal. Cooling of the gas is largely dependent on the temperature of the cooling water which in turn is a function of atmospheric temperature, relative humidity, and the capacity of the water cooling system. It is not uncommon to find these water cooling systems overloaded in the summer or at peak production. Introduction of cool water into the recirculating system during such periods may cause overflow or additional discharge of these highly pollutional wastes, (Table 5).

Water soluble substances are absorbed in the final cooler water and build up in concentration as the water is recirculated. This is especially true if alkaline chemicals are added as was the case at Plant D. Sulfides are normally driven off in the cooling tower or they are converted to thiosulfates and thiocyanates. Cyanogen compounds build up to a moderate degree but most of the cyanide escapes in the cooling tower. The amounts of waste constituents removed from the gas decrease as their concentrations increase in the recirculated final cooler water. This is reflected in the benzol plant effluent for Plants E-1, H-1, and H-2 where phenols and cyanide were efficiently scrubbed from the gas in the once-through final cooler and by the ammonia scrubbers of the indirect system.

Cooling Water

Indirect cooling water is not normally considered waste but leaks in coils or tubes may be a significant source of pollutional materials. This applies to any cooling system in which the process stream is under greater pressure than the cooling water. Leakage of ammoniacal liquor through these coils at one plant amounted to 6 gallons per minute. This represented 60 pounds phenols per day as well as considerable ammonia.

TABLE 5
GAS FINAL COOLER WATER
CONCENTRATIONS OF POLLUTIONAL CONSTITUENTS
FOR THREE TYPES OF COOLING SYSTEMS

		COOLING TOWER AND RECIRCULATION (CLOSED SYSTEM)			COOLING WATER DIRECT TO SEWER		COOLING COILS-CONDENSATE TO SEWER
Plant		B	C	D*	E-1	E-2	E-3
Phenols	Parts Per Million	1140	250	1700	5	3.8	380
Cyanide (CN)		140	220	270	160	26	200
Sulfides (H_2S)		16	3	1125	10	-	-
Thiocyanate (SCN)		140	290	3340	-	-	730
5-Day BOD		2890	-	-	495	425	-
Flue Temperature	°F	2325	2500	2550	2250	2020	2200
Flow to Sewer	Gallons Per Ton Dry Coal	None	None	None	1400	2420	5.8

* Soda ash added to reduce sulfide concentration of gas sold for domestic use.

Coke Quench Wastes

Quenching of coke requires some 500 gallons of water per ton of coke. Roughly 30 per cent of this water is evaporated by the hot coke and is carried into the air as a white cloud emanating from the quench tower. Hot water draining from the coke flows to a settling basin for removal of coke fines. The settled water either overflows to the sewer or is recirculated. When fresh water is used for quenching, traces of pollutional materials are picked up from the coke but increase in temperature is the principal objectionable feature of the settled waste.

Miscellaneous Wastes

The volume and character of miscellaneous wastes are a function of equipment design and maintenance, and of operation. Provision is usually made for salvage of materials when equipment and process pipe lines must be drained. Nevertheless there are numerous losses to the sewers which are associated with operation. Equipment maintenance and good housekeeping are both major factors affecting such losses.

Coke Plant - Total Wastes

Effluent data for 8 different by-product coke plants are given in Table 6. Interpretation of these results requires background information which has been given in the preceding tables and accompanying discussion. The most striking results are for Plant B where benzol plant wastes and dephenolized ammonia still wastes were used for quenching coke. Cooling water was recirculated and the only discharge from Plant B was intermittent overflow from the quench system caused by inadequate storage.

TABLE 6
CONCENTRATIONS AND QUANTITIES OF POLLUTIONAL CONSTITUENTS IN BY-PRODUCT COKE PLANT WASTES

AMMONIA RECOVERY PROCESS		SEMIDIRECT			INDIRECT					
DEPHENOLIZATION SYSTEM		VAPOR RECIRCULATION		BENZOL EXTRACTION	NONE					
Plant		A-2	B	C	D	E-1	F-2	G	H-1	H-2
Phenols	Parts Per Million	1.9	280	1.9	25	11	34	29	17	11
Cyanide (CN)		0.35	6.0	0.66	0.54	155	0.15	1.7	0.14	0.20
Total NH_3 (N)		2.5	25	1.5	7.4	78	1.5	8.4	2.3	-
Thiocyanate (SCN)		-	73	9.3	-	-	12	-	-	16
5-Day BOD		-	990	-	94	520	-	63	63	-
Phenols	Pounds Per 1000 Tons Dry Coal	48	9	14	340	132	1170	660	480	330
Cyanide (CN)		8.7	0.2	5	7.5	1850	5	39	4	6
Total NH_3 (N)		62	1	10	100	920	50	90	65	-
Thiocyanate (SCN)		-	2	67	-	-	420	-	-	490
5-Day BOD		-	32	-	1300	6150	-	1320	1800	-
Volume	Gallons Per Ton Dry Coal	2960	4	860	1650	1420	4100	2740	3450	3670

POLLUTIONAL EFFECTS

Taste and odor producing properties of by-product coke wastes are of foremost concern. They contain significant quantities of chemicals known to be toxic to aquatic life. These wastes exert a considerable oxygen demand on receiving waters. Elevation of stream temperature by the warm discharge inhibits aquatic life and limits immediate reuse of the stream for cooling purposes.

Taste and Odor

The phenolic constituents of by-product coke wastes have long been associated with taste and odor in drinking water. Phenol itself is not taste producing in low concentrations, however its importance in this regard stems from the fact that chlorination increases the taste intensity. It has been demonstrated in the laboratory that the intensity of the taste of pure phenol in water is increased 500 to 1000 times by chlorination. Fortunately the maximum taste intensity is developed only at certain critical ratios of chlorine to phenol and excess or break-point chlorination, as practiced at most water purification plants, is quite effective in reducing the taste intensity. The chlorophenol taste is commonly described as "medicinal" and is particularly unsavory. People with average taste sensitivity can detect chlorophenol in water in concentrations of the order of 1 to 2 parts per billion. Both the 4-aminoantipyrine and the Gibbs Methods determine not only phenol but also cresol and a variety of phenolic compounds most of which are similar to phenol in taste and odor producing properties.

Less is known about the taste and odor potential of constituents, other than phenol, in by-product coke wastes. The Sanitary Engineering Center has done some preliminary work on ammonia still waste, from a plant using the Koppers vapor dephenolization system, by extraction with diethyl ether and separation of

strongly acidic, weakly acidic, neutral, and basic compounds. These observations indicated that the weak acid fraction, which contained the preponderance of residual phenolic materials, was somewhat overshadowed in its contribution of odor by the strong acids, neutrals, and bases. Although chlorination reverses this relation, it appears that non-phenolic materials have some significance in the residual wastes from by-product coke plants. It further appears that when other organic materials are present in water the multifold increase in odor intensity exhibited by pure phenol, following chlorination, is of lesser magnitude. The results of these studies strongly suggest the need for evaluating both phenolic and non-phenolic constituents in coke plant wastes to accurately estimate their taste and odor producing potential.

Toxicity of Components to Aquatic Life

By-product coke wastes contain numerous chemical compounds which are known to be toxic to aquatic life in low concentrations. These include cyanide, sulfides, ammonia, and phenols. Other highly toxic materials which may be present in significant concentrations are toluene, benzene, acridine, quinoline, and naphthalene. Process wastes that have been in contact with coal tar and the light oils may be expected to carry traces of a great variety of compounds. Information is available and summaries have been published indicating the toxic effects of many of these compounds on fish (6) (7) (8) (9).

Hydrocyanic acid (HCN) and its salts are among the most violent poisons known. The most potent source of HCN in coke plant wastes is the gas final cooler water (Table 5). This is reflected in Plant E, Table 6, which plant used the once-through gas final cooler system and discharged a considerable quantity of cyanide.

The toxicity of cyanides is affected by the proportion of cyanide ion to

the undissociated molecule. HCN is more toxic than the equivalent concentration of hydrogen and cyanide ions. Hydrocyanic acid forms in water when either NaCN or KCN is added. The HCN dissociates into hydrogen and cyanide ions according to the reversible reaction.

$$HCN \rightleftharpoons H^+ + CN^-$$

The dissociation constant for HCN is 7.2×10^{-10} at 25° C., therefore the ratio of cyanide ion to HCN is a function of pH as follows:

$$\frac{[CN^-]}{[HCN]} = \frac{7.2 \times 10^{-10}}{[H^+]}$$

It is evident that cyanide becomes more toxic at the lower pH values.

Available information indicates that cyanide (CN) should not exceed 0.05 ppm in receiving waters. Under certain conditions, somewhat lower values may have a detrimental effect on aquatic life.

Hydrogen sulfide in concentrations of 1 to 6 ppm has been reported lethal to different kinds of fish under variable water quality conditions. Other sulfides such as Na_2S are hydrolyzed in solution yielding hydrogen sulfide. The pronounced toxicity of solutions of sulfides may be attributed to release of H_2S as the pH is lowered. For protection of aquatic life, H_2S in receiving waters should not exceed 0.5 ppm.

The toxicity of ammonia and ammonium salts to fish is directly related to the amount of undissociated ammonium hydroxide in solution, which in turn is a function of pH. Ellis has reported that the toxicity to fish of a given concentration of ammonium compounds, increased 200 per cent or more when the pH was raised from 7.4 to 8.0 (7). Available data indicate that ammonia in excess of 2.0 ppm, in the pH range of most natural waters, may be expected to affect aquatic life. Concentrations above 2.0 ppm may be non-toxic and values

below can be toxic, depending on the characteristics of the receiving stream.

Phenols in excess of 5 ppm may be expected to be toxic while concentrations of 1 ppm or less will probably be safe; however, some chlorophenols are toxic below this level. Sub-lethal concentrations of various phenolic compounds impart an offensive taste to fish flesh.

Following are concentrations reported lethal to fish for certain materials likely to be present in coke plant wastes (6) (7) (10).

	Parts Per Million
Cresylic Acid	0.1
Acridine	0.7
Naphthalene	4 to 10
Naphthenic Acid and Naphthene Derivatives	3 to 20
Quinoline	7.5
Benzene	20
Toluene and Xylene	22 to 90

The above results represent short time exposure of various types of fish. These concentrations would have to be reduced substantially to permit normal aquatic life in a stream.

Ferro and ferri-cyanides are normally non-toxic below 2000 ppm. However, in bright sunlight, 2 ppm of these compounds may be toxic because of photo-decomposition and release of the cyanide ion (11). Similarly, thiocyanates which are usually non-toxic below 150 ppm may become toxic at levels as low as 6 ppm when chlorinated to a slight residual as a result of release of cyanide or the formation of cyanogen chloride.

Bio-Assay Studies

The foregoing information on toxicity must be used with caution because

biological data are not adaptable to rigid application. In some wastes one toxic constituent may predominate while in others toxicity may result from the combined effect of several components. These in admixture or under the influence of non-toxic constituents may exert an entirely different degree of toxicity from the separate compounds. Bio-assays are extremely helpful in estimating the toxic effect on fish of complex industrial wastes.

The bio-assay procedure used on coke plant wastes consisted of preparing several concentrations of the waste using the receiving stream water for dilution, adding test fish, and observing their reaction over a definite time period (12). Test fish were fathead minnows, Pimephales promelas. Toxicities were expressed as median tolerance limits (TLm), which were the concentrations of the wastes in dilution water which killed half the fish in 48 hours.

Bio-assays of five, 8 hour composite samples of the final effluent from one by-product coke plant gave 48 hour TLm values ranging from 4 to 14 per cent with an average of 7.5 per cent. Typical analysis of the dilution water showed 95 ppm total alkalinity, 125 ppm versenate hardness, and pH of 8.2.

In an effort to evaluate the toxic effect of some of the known components in these wastes, bio-assays were run on pure compounds under the same test conditions. The results in Table 7 show that these compounds account for only a small part of the toxicity in the final effluent. It is evident that other unknown materials of a highly toxic nature were present or that there was a strongly synergistic action between some known components.

Concentrated wastes inside the plant were examined by bio-assays to reveal significant sources of toxic materials. This work gave the following data:

TABLE 7

BIO-ASSAY RESULTS ON SOME TOXIC CONSTITUENTS IN BY-PRODUCT COKE WASTES

Pure Compounds		Chemicals in Final Effluent	
Compound Tested	48 Hour TLm Concentration - ppm	Constituent	Range of Concentration ppm
Sodium Cyanide NaCN	0.24 (CN)	Cyanides (CN)	0.02 - 0.30
Ammonium Hydroxide NH_4OH	7 (N)	Free Ammonia (N)	5.8 - 11
Phenol C_6H_5OH O-Cresol $CH_3C_6H_4OH$	40 24	Phenols	37 - 48
Sodium Sulfide $Na_2S \cdot 9H_2O$	1.38 (H_2S)	Sulfides (H_2S)	0.51 - 1.15

Source of Waste	48 Hour TLm Per Cent
BTX Caustic Wash	0.15
Ammonia Still Waste	1.25
Light Oil Decanter Discharge	2.5
Gas Final Cooler Recirculating Water (Normally no overflow to sewer)	0.7

Bio-assays of ammonia still wastes from a coke plant that dephenolized the ammoniacal liquor by solvent extraction gave a 48 hour TLm of 7.5 per cent. This indicates considerable reduction in toxicity. Phenols are not considered a major producer of toxicity in coke plant effluents, however, it is possible that other toxic materials are removed by dephenolization.

Care must be exercised in the application of bio-assay data. The concentrations expressed as TLm values will kill 50 per cent of a fairly hardy test fish in a short time period. Obviously these concentrations would not be considered safe for aquatic life. Liberal factors must be used in applying the results. A completely safe concentration may be as little as one tenth of the 48 hour TLm value. These studies demonstrated the value of bio-assays in tracing sources of toxic components of wastes within a plant and served to emphasize the highly toxic nature of by-product coke effluents.

Dissolved Oxygen Depression

Coke plant effluents have a significant biochemical oxygen demand and may damage fish by oxygen depression. Some chemicals, especially those which affect the gills, are much more toxic under low oxygen conditions. Sufficient oxygen must be available to support normal life processes such as obtaining food, swimming against currents, and reproduction. Temperature, carbon di-

oxide, and stream velocity, all affect the oxygen requirements of fish. The dissolved oxygen concentration should be 5.0 ppm or higher to maintain a desirable mixed warm water fish population.

Temperature Increase

The elevation of stream temperatures by discharge of coke plant wastes may have a serious effect on aquatic life. The toxicity of many chemicals to fish is increased by increasing the water temperature. Likewise the metabolic rate and oxygen requirements of fish increase with temperature rise. Fish food organisms may also be affected. Most fish have definite temperature limits between which they will spawn. Water temperatures of 95° F. for most species of warm water fishes and 83° F. for trout approach lethal levels. Maximum temperatures of extended duration should be considerably lower than these and abrupt changes of even a few degrees should be prevented if aquatic life is to be protected.

REMEDIAL MEASURES

Remedial measures should be directed toward prevention of tastes and odors in public water supplies and protection of aquatic life. In the past, emphasis has been placed on phenolic compounds because of their effect on drinking water. However, efficient removal of phenols from coke plant wastes does not solve the toxicity problem. Though interrelated, tastes and odors, and toxicity are two distinct problems. This discussion is confined to generally accepted recovery and treatment methods. An excellent literature review and bibliography covering recovery and treatment methods for by-product coke wastes has recently been published by Hodge (13).

Dephenolization of Ammoniacal Liquor

Recovery of phenols from ammoniacal liquor, though not economically sound, offsets the cost of pollution abatement. The economics is strongly in favor of synthetic processes which account for some 95 per cent of the phenol produced in the United States (14). Two processes are in common use for dephenolization, namely: solvent-extraction and Koppers vapor-recirculation.

Benzol or light oil extraction has been used extensively in Germany and in recent years has gained favor in the United States. In this process the ammoniacal liquor is intimately contacted with benzene in a countercurrent extraction system prior to entering the ammonia still. This is a desirable feature from the standpoint of wastes inasmuch as the maximum amount of phenols are promptly removed.

A general flow diagram of the benzol countercurrent type of dephenolization process is shown in Figure 5. Filtration of the liquor through porous stone

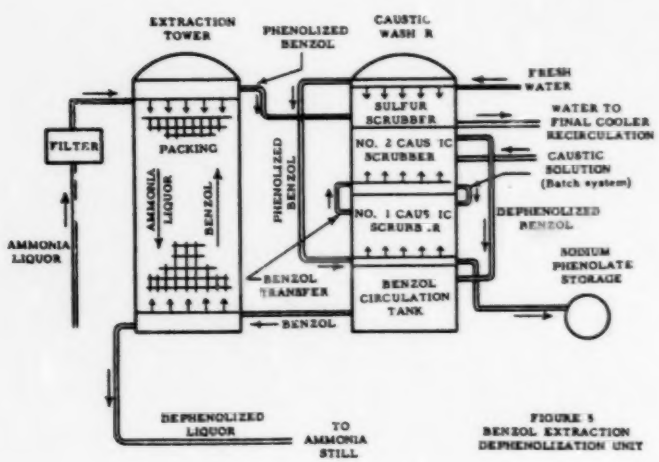


FIGURE 5
BENZOL EXTRACTION DEPHENOLIZATION UNIT

removes tar and suspended material. The two contact towers are packed with screened coke, wooden hurdles, or spiral tile. The benzol flows upward, absorbing phenols from the descending ammoniacal liquor, and overflows at the top of the extraction tower. The dephenolized liquor flows to the ammonia still. Phenol bearing benzol flows through a two stage, packed contact tower containing a solution of 20 to 30 per cent caustic soda to produce sodium phenolate. The sulfur scrubber shown in Figure 5 is used in some plants. The benzol recycles through both towers acting as a carrier medium for phenols. Sodium phenolate is salable or it may be converted to phenol by acid treatment.

The principal factors affecting efficiency of benzol extraction are temperature, solvent-liquor ratio, and intimacy of contact between the two liquids. The efficiency declines with decrease in the benzol-liquor ratio. A recently constructed plant consistently gives 98 to 99 per cent phenol removal using 1.5 gallons of solvent per gallon of liquor (15).

One of the major causes of decreased efficiency is the formation of emulsions which results in blockage of packing and lines. Emulsions are attributed to absorption of tar in the circulating benzol. This can be alleviated by continuous withdrawal of fouled solvent and replacement with fresh light oil. The portion withdrawn is distilled to recover the benzol.

German dephenolization practice emphasizes pretreatment (16). The liquor is first filtered through sand and then is passed through a column filled with benzol. This benzol is soon saturated with phenol after which it continues to absorb organic material and neutral oils for a period of 3 to 10 days. Benzol employed in pretreatment is suitable, after distillation, foruse in the principal extraction. Advantages claimed for this system are: elimination of emulsions, less benzol required, and minimum solvent loss. This preliminary treat-

ment permits solvent-liquor ratios as low as 1 to 1 and gives phenol removal efficiencies in the low nineties.

Recent developments in liquid-liquid extraction, applicable to dephenolization of ammoniacal liquor, include the Podbielniak centrifugal extractor and the Shell Development Company rotating disk contactor. Both devices provide maximum intimacy of contact between the two liquids and give high efficiencies.

The vapor recirculation process is illustrated in Figure 6. Liquor from the base of the free leg of the ammonia still is sprayed into the top of the tower. It flows down over wooden-hurdle packing countercurrent to a large volume of low pressure steam. Due to the vapor pressure of the phenol, it passes into the steam. The dephenolized liquor flows by gravity to the fixed leg of the ammonia still. The blower draws the phenol laden steam from the top of the tower and discharges it into the lower or caustic section where it is scrubbed with caustic. The phenol free steam reenters the dephenolization section to complete the cycle. The phenol is recovered as sodium phenolate.

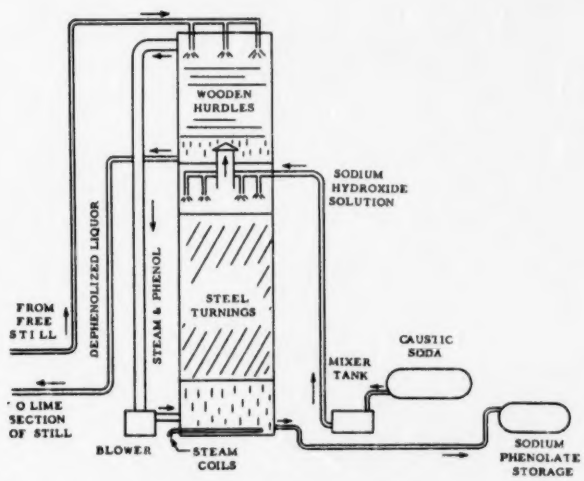


FIGURE 6. KOPPERS VAPOR - DEPHENOLIZATION SYSTEM

Feed to the vapor recirculation system is taken from the base of the free leg of the ammonia still to avoid the acidic gases, carbon dioxide, hydrogen sulfide, and hydrogen cyanide which would react with the caustic. Free ammonia and a considerable amount of phenol are stripped from the ammoniacal liquor along with these gases in the free leg of the still. This phenol, which carries into the gas stream, builds up in the gas final cooler water and some appears in the benzol plant wastes as shown for plant B in Tables 3 and 5.

Performance tests run on four plants gave the following results based on feed to and discharge from each dephenolization unit:

Dephenolization Process	Benzol Extraction		Vapor Recirculation	
Plant	A-3	C	A-2	B
Phenol Removal (per cent)	98.4	90.9	87.1	70.2

Consumption of Wastes by Coke Quenching

Disposal of ammonia still wastes by coke quenching is practiced at a large number of coke plants in the United States. This method of disposal is certainly the most effective and complete because it not only controls phenols but also all other pollutional constituents. This may be especially important in view of the taste and odor potential, and the toxic effects of these wastes. Figure 7 shows a coke quenching system for disposal of all liquid wastes from a by-product coke plant.

A completely closed system is necessary with provision for recirculating the water which drains from the coke. This retains all coke breeze and removes a high temperature discharge from the sewers. Sufficient storage should be provided in the quench water system to store wastes for periods such as shift changes when pushing of ovens is temporarily suspended. The addition of fresh water to the system should be controlled so that wastes are preferentially used for the quench rather than the supplemental supply.

Some of the materials in the water of a closed quench system (Figure 7)

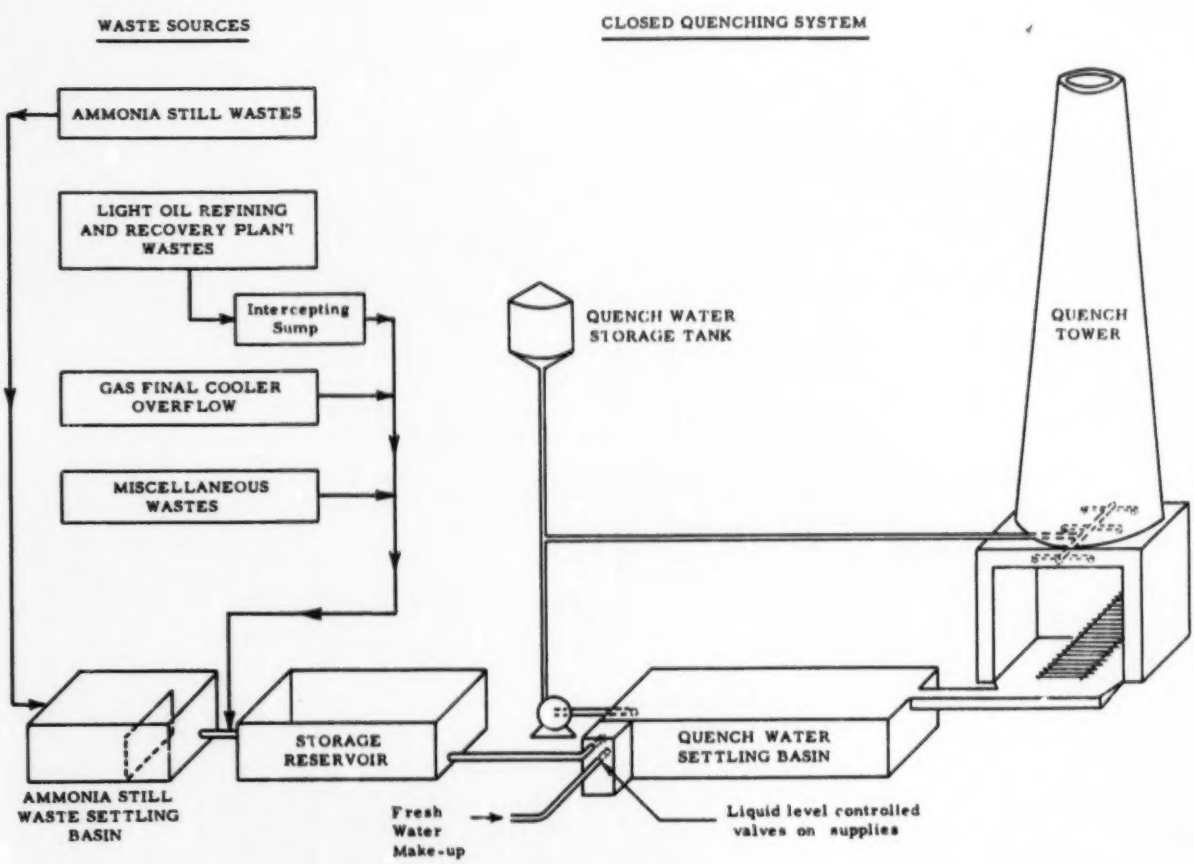
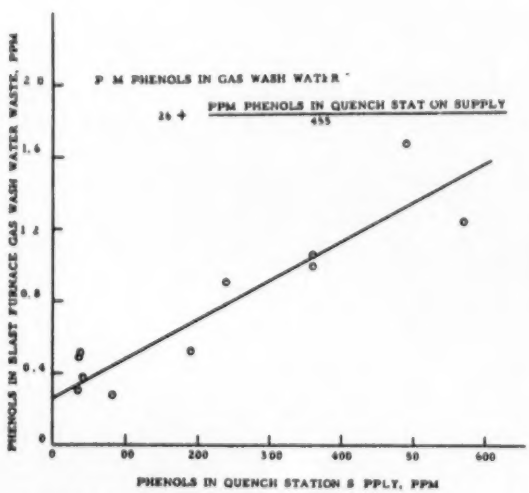


FIGURE 7

COKE QUENCHING SYSTEM FOR DISPOSING OF ALL LIQUID WASTES

are entrained in and deposited on the coke. The phenolic odor and the discoloration from deposition of salts preclude domestic use of such coke. These changes in the coke are likewise reflected in the blast furnace department. It has been suggested that deterioration of blast furnace lining may be accelerated by use of coke quenched with the high chloride still waste. Phenolic materials entrained in the coke appear in the blast furnace gas wash water as shown in Figure 8. These data were obtained by varying phenols in the quench water and measuring phenols in the blast furnace gas wash water when this contaminated coke was a part of the furnace charge. Correlation of blast furnace operations with coke waste data indicate that phenol carryover in the blast furnace gas wash water may be expected to vary between 5 and 10 per cent of the phenolic content of the coke quench water (17).



FIGU 8 RE ATIONSHIP OF PHENOLS QUENCH STATION SUPPLY AND BLAST FURNACE GAS WASH WATER WASTE

Quenching coke with waste waters is beset with other objectionable features. The corrosive effect of these wastes, because of their chloride content, is apparent on all metal surfaces with which they come in contact. Monetary damage, though difficult to assess, must be charged to this method of waste disposal. The contaminated vapors emanating from the quench tower may create an air pollution problem in a congested or built up area.

Biological and Chemical Oxidation

Biological treatment of waste liquors from coal carbonization processes has been practiced extensively in England and to a limited extent in the United States for many years (9) (13) (18) (19). Although gas works liquor common to England is not identical with by-product coke wastes, they possess very similar characteristics. The wastes can be combined with domestic sewage and treated in conventional treatment works. The Milwaukee and Chicago activated sludge treatment plants both receive coke plant wastes. In England, much of the combined sewage is treated on percolating filters with the volume of gas works liquor being held to 0.5 per cent of the volume of combined wastes. Combined treatment has proven satisfactory where there was adequate domestic sewage.

Dephenolized ammonia still waste has been subjected to chemical oxidation on pilot plant scale (20). Chlorine, ozone, and chlorine dioxide were used in this experimental work. The efficacy of treatment was demonstrated but the cost for full scale development was considered prohibitive.

ANALYTICAL METHODS

Evaluation of the wastes discharged in the various phases of by-product coke operations makes it necessary to determine a number of chemical entities.

Of these chemical components, phenols and cyanides are especially important. The analytical procedures for these materials have undergone revision as a result of research since the start of our coke waste studies. A brief summary of the various modifications used, together with a short discussion of their merit will be given.

Phenol Determination

Three methods were used in the determination of phenols in by-product coke wastes. These methods consisted of Scott's bromination procedure, Gibb's chlorimetric method using 2,6 - dibromoquinonechlorimide, and the 4 aminoantipyrine method as originally proposed by Emerson. The modifications of this latter method as well as the other two methods are contained in the Tenth Edition of "Standard Methods for the Examination of Water, Sewage, and Industrial Wastes."

In the use of any of the methods mentioned above it is first essential that the phenolic compounds be separated from any compounds that might cause either positive or negative interference with the method. The screening procedure usually used, regardless of the analytical method of choice, may be briefly summarized as follows.

The sample is distilled from an acid solution in the presence of copper sulfate, which theoretically should eliminate nitrogen base compounds, sulfides and high boiling organic compounds (these latter compounds may also consist partially of high boiling phenols). The phenols together with the organic acids and neutral compounds are extracted from the acid distillate with chloroform. The chloroform is then serially extracted with sodium hydroxide leaving the neutral compounds in the chloroform layer. A further purification step has also been used in some cases by distilling the caustic extract

from an acid solution, again in the presence of copper sulfate. By the use of this screening procedure the phenolic compounds present in the original sample should be relatively free from interfering substances.

In using the bromination procedure for determining phenols it is doubly important that no compounds be present (except phenolic) which would react with bromine, since this test is essentially a bromine-demand test. Typical examples of such compounds which may be found in coke wastes are organic nitrogen bases, sulfides, ammonia, cyanides, etc. In using the bromination method it is necessary to follow the detailed procedure as outlined by Scott, otherwise the data obtained may not be comparable to that obtained by the other methods. In the hands of a competent analyst this method is shown to yield reasonably close check results with the Gibbs procedure on such wastes. These data are given in Table 8.

The method which has been most frequently the one of choice is the Gibbs colorimetric procedure. It is necessary to adequately screen the sample to remove interfering components. This is particularly true of reducing compounds such as sulfides. If the complete screening procedure is used there may be phenolic compounds present in the final distillate which will not react with the Gibbs reagent. This is true of those phenolics which have a group (other than chlorine) substituted in a position para to the hydroxyl group.

Another important factor which enters into the determinations of phenolics by the Gibbs procedure is the sensitivity of this reaction to pH control. Fading of the color or complete decolorization will follow if the pH is allowed to fall below 9.2. The data in Table 8 show that if an adequate screening procedure is followed, plus the proper analytical control, check results can be obtained on wastes from the coke industry.

TABLE 8

COMPARISON OF PHENOL RESULTS DETERMINED
BY BROMINATION AND BY GIBBS METHODS
FOR VARIOUS BY-PRODUCT COKE WASTES

	Scott's Bromination (p.p.m.)						Gibbs (p.p.m.)					
Sample No.	1	2	3	4	5	6	1	2	3	4	5	5
Ammonia Still *	264	356	262	350	949	957	246	458	126	257	915	1000
North Quench	4.0	9.7	-	4.0	1.0	-	1.0	1.0	-	1.4	1.0	-
North Outfall	8.5	8.5	6.0	13.0	16.	9.9	7.0	8.5	4.0	16.0	25.0	8.9
Intercepting Sump	308	324	533	328	353	266	292	388	306	292	335	298
Main Outfall	10.0	13.3	14.5	13.0	13.0	66	28	13.5	11.0	19	13.0	71
Final Cooler Water	356	434	380	368	424	399	329	420	400	334	342	312
Ammonia Still *	590	576	569	658	658	695	524	629	545	798	782	550

* Different By-Product Coke Plants

The third method that was used in the latter coke plant studies was the 4-aminoantipyrine procedure. This method can be carried out in less time than either of the others and may be adapted to high or low concentrations of phenols. Again as with the other two methods an adequate screening procedure must be used. As mentioned previously, in the Gibbs procedure para substituted phenols are not determined, while with 4-aminoantipyrine, if the para substituted group is a halogen, carboxyl, hydroxyl or sulfonic acid, a positive reaction is obtained.

Comparative checks for phenols were made by the Gibbs and 4-aminoantipyrine methods on one coke plant effluent. The results are tabulated below:

Sample No.	4-aminoantipyrine ppm	Gibbs ppm
1	40	34
2	17	13
3	47	49

In addition to the results given above, ammonia still waste has been analyzed for phenol at the Center's laboratories by both the Gibbs and 4-aminoantipyrine methods on several occasions. On all of these samples the two procedures gave consistent checks on this particular waste.

Cyanide Determination

In the earlier coke plant studies, the tartaric acid distillation method was used and the cyanide absorbed in caustic was titrated with standard silver nitrate. This procedure is effective in the breakdown of simple cyanides but with complex cyanides the breakdown is less than by using the Serfass reflux procedure. With the type of cyanide components encountered in by-product coke wastes little difference would be expected in the results obtained in the two

distillation methods. When the cyanide concentration was above 1.0 ppm, it was determined by titration, below this concentration the pyridine - pyrazalone colorimetric procedure was employed.

AREAS FOR RESEARCH

These studies have revealed numerous areas for research. These include:

1. Identification of constituents responsible for toxicity to aquatic life.
2. Determination of the nature and persistence of non-phenolic taste and odor producing materials.
3. Development of control or treatment methods to reduce the toxic and taste and odor characteristics.
4. Assessment of the damages claimed for quenching coke with by-product coke wastes.

SUMMARY AND CONCLUSIONS

The research on which this guide is based has contributed to a greater understanding of the factors which influence by-product coke wastes and of their effects on receiving waters. Analysis of the data collected during these several research projects leads to the following summary statements and conclusions:

1. The quantity of pollutional materials in ammoniacal liquor varies directly with the volatile matter in the coal charged to the ovens.

2. Temperature of carbonization has a significant effect on production of phenols and cyanogen compounds; phenols decrease and cyanides increase with rise in coking temperature.

3. Pick up of pollutional material by the ammoniacal liquor, in the indirect ammonia recovery process, can be greatly reduced by preventing con-

tact of ammonia scrubber water with flushing liquor.

4. Solvent extraction dephenolization systems can be designed and operated to remove over 98 per cent of phenols from raw ammoniacal liquor thereby preventing carry over of phenols to the gas stream and to subsequent processes.

5. Gas final cooler water is a highly pollutional liquor but through use of cooling towers and closed systems this liquor normally does not enter the sewers.

6. Benzol plant process wastes, though relatively small in volume, are highly toxic and may account for a significant portion of the toxicity observed in coke plant effluents.

7. It is possible to dispose of all liquid wastes in a closed coke quench system, however, some of the phenolic materials are absorbed by the coke and reappear in the blast furnace gas wash water.

8. Ammonia still wastes are amenable to biological treatment when combined with relatively large volumes of domestic sewage.

9. It is necessary to evaluate both phenolic and non-phenolic constituents in coke plant wastes to accurately estimate their taste and odor potential.

10. The toxic nature of by-product coke effluents has been demonstrated and several highly toxic component wastes have been examined.

ACKNOWLEDGEMENTS

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